



Research paper

Hygienic aspects of TiO₂-mediated photocatalytic oxidation of volatile organic compounds: Air purification analysis using a total hazard index

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ABSTRACT

The purification of air polluted by volatile organic compounds (VOCs) using the TiO₂-mediated photocatalytic oxidation (PCO) method was analyzed from a hygienic point of view by the evaluation of the total hazard during the process. For this purpose, the photocatalytic oxidation of various VOCs, including acetone, alcohols, hydrocarbons, and heteroatomic compounds, was investigated in a static reactor using an FTIR *in situ* method for the identification and quantitative analysis of the reaction components in the gas phase. The change in hazards during the PCO process was calculated using two hazard indexes, the maximum hazard quotient (MHQ) and the total hazard index (THI), which include the contribution of all the reaction components and be the quantitative characteristics for the estimation of the PCO purification efficiency from a hygienic point of view. The results for all the VOCs considered showed the fundamental ability of the PCO method to decrease the hazards in polluted air. The hazard indexes depended on the UV irradiation time and the type of VOC. For VOCs that are photocatalytically oxidized without the formation of gaseous intermediates, the hazard indexes initially decreased as the concentration of the VOC decreased but then slightly increased at the end of the PCO process mainly due to the accumulation of CO, which was formed as a final by-product. The TiO₂ modification with Pt was shown to completely or partially suppress CO accumulation during the PCO process and to increase the efficiency of air purification from a hazard index point of view. For the photocatalytic oxidation of VOCs that results in the formation of gaseous intermediates, the hazard may increase during the PCO process and even be much higher than the initial level because such intermediates (i.e., aldehydes, acids, and inorganic compounds) have extremely low threshold limit values. Under long-term UV irradiation, all the intermediates were completely oxidized, and the hazard levels substantially decreased compared to the initial level.

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1. Introduction

A high level of emissions from industry, energy production, and motor transport results in substantial air pollution containing carbon monoxide, sulfur and nitrogen oxides, VOCs, and other compounds worldwide. The World Health Organization (WHO) reported in 2012 that ca. 6.5 million people die every year due to diseases that are directly or indirectly caused by polluted air [1]. The development of effective methods for air purification is an important task to ensure human safety and environmental sustainability.

The photocatalytic oxidation using TiO₂-based photocatalysts has attracted great attention in the last several decades as a method

for the removal and complete degradation of gaseous pollutants, including VOCs and some inorganic gases [2]. The degradation occurs due to the oxidation of the pollutants by highly reactive species that form on the photocatalyst surface under irradiation. Photocatalysts based on bare TiO₂ can only absorb light in the UV region because TiO₂ is a semiconductor material with energy band gaps of 3.0 and 3.2 eV for the rutile and anatase crystal phases, respectively [3]. Additionally, various modifications of TiO₂ are being extensively developed to extend the photocatalyst absorption into the visible region for more efficient utilization of solar light [4–7].

The photocatalytic oxidation of many types of organic compounds, including alkanes, alkenes, alkynes, aldehydes, aromatics, alcohols, and ketones, has been investigated [8–12]. Compounds containing heteroatoms (e.g., N, S, P, Cl) have also been photocatalytically oxidized over TiO₂-based catalysts [13–15]. In many

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cases, researchers are only focused on removing the initial pollutant and do not consider the oxidation products formed. The PCO process occurs through the gradual oxidation of the initial pollutant, and some intermediates can be released to the gas phase [16]. The typical intermediates and by-products formed during PCO for some types of VOCs were summarized by Mamaghani et al. in a recently published paper [17]. The formed intermediates can be even more hazardous than the initial pollutant. In addition to the organic intermediates and by-products, we have shown that carbon monoxide always forms as a final by-product along with CO₂ and water during the photocatalytic oxidation of VOCs over TiO₂ [18–20].

The results described above indicate that the PCO process may be a source of secondary pollution, and it is necessary to properly analyze the change in the total hazards during the PCO purification process. The approach should consider the hazards for the initial pollutant and intermediates, as well as the possible hazards of the final products.

A worldwide method used for ranking hazardous compounds is based on the determination of a reference concentration for individual compounds at which no significant impact on human health is observed. The most common ranking is based on the WHO guidelines [21]. However, the list of compounds mentioned in the guidelines is very short, and the suggested approach is hardly suitable for the quantitative determination of the hazard of a mixture of specific chemical compounds.

Many countries have their own specific standards for governing the content limit of hazardous compounds in the air. For example, the content limit for air pollutants in Russia is governed by hygienic standards (GN 2.1.6.1338-03) in the residential area and GOST 12.1.005-88 in the workplace. Specific documents for limits in the workplace can be found in other countries too, e.g., technical rules for hazardous substances (TRGS 900) in Germany, EH40/2005 workplace exposure limits in the UK, workplace environmental exposure level values by the American Industrial Hygiene Association (AIHA) and threshold limit values by the American Conference of Governmental Industrial Hygienists (ACGIH) in the USA. Many standards and governing acts operate with threshold limit values (TLVs) or other indicators based on the same principle. TLV is the maximum concentration of a chemical compound that a worker can be exposed to for a specified time period (e.g., 8 h or 15 min) without adverse health effects. The TLV values issued by the ACGIH are widely accepted.

However, the question about the usage of TLV values for gas mixtures, which change during a chemical process, is still open. Koller et al. [22] have proposed a method that may be employed during process development to evaluate the impact of the process on the safety, health, and environmental (SHE). The method calculates the common potential hazards and considers 11 categories of possible impact (i.e., toxicity, light irradiation, solid wastes, air- and water-mediated effects, etc.). This method has been further adopted and employed in other studies for the selection of a chemical process route by calculating an integrated inherent chemical process route index (ICPRI) [23].

Hassim and Hurme [24–26] have also developed an inherent occupational health index (IOHI) to evaluate the health risk for different process routes during development and a health quotient index (HQI) to provide an approach to quantify health risks for workers exposed to volatile pollutants. Combining all the possible factors into one specified index is the fundamental idea of these methods. They are based on only the properties of the compounds and the operating conditions, which are available in the early stages of the process development, but these approaches are too general and not precise enough for the analysis of a gas mixture that changes during the process.

Another widely accepted concept for the analysis of air pollution hazards is the determination of hazard quotient (HQ), which is the ratio of the concentration of an individual compound to the reference concentration, which corresponds to a limit of this compound. HQ can be expressed as follows:

$$HQ = \frac{C}{C^{ref}} \quad (1)$$

where C and C^{ref} are the apparent and reference concentrations of the pollutant, respectively.

TLV or other threshold limits that are more suitable for the considered conditions are used as the reference concentrations. It is important to note that some compounds (e.g., ammonia, hydrogen sulfide, and formaldehyde) can have a so-called “cocktail effect” due to their similar actions on human health, which increases the impact of each compound [27]. In this case, the HQ should include all the components in the “cocktail effect” as follows:

$$HQ_c = \sum_j \frac{C_j}{C_j^{ref}} \quad (2)$$

The chemical process is a mixture of compounds, and the total hazard can be estimated either as the maximum HQ among all the compounds with no additive effect among the components or as the sum of the HQ values for all the compounds, which corresponds to an additive effect of all the components in the mixture (i.e., the worst-case scenario) [28]. In the latter case, the total hazard is also called the hazard index (HI) and can be expressed as follows [29]:

$$HI = \sum_i HQ_i = \sum_i \frac{C_i}{C_i^{ref}} \quad (3)$$

where HQ_i is the hazard quotient for the i^{th} component, C_i is the concentration of the i^{th} component, and C_i^{ref} is the reference concentration of the i^{th} component. The similar concept has been also proposed by Hollick and Sangiovanni and called as tolerance index [30].

The prediction of a possible interaction between different compounds requires expert judgment and needs to be considered on a case-by-case basis. For example, according to the current EU legislation, the assessment of an additive effect for exposure to multiple chemicals is required only in a few instances (e.g., for pesticides) when a suitable methodology is available [27]. On the other hand, WHO states that if no information about an additive action is available, the dose addition method (i.e., Eq. (3)) is preferable to the independent action method (i.e., a maximum HQ) [31].

Additional numerical coefficients, including the inhalation rate, human body weight, exposure time, and frequency, can be used for more specific calculations of hazard indexes.

The HI approach is more suitable for the evaluation of a time-weighted average accumulated risk and does not show an alarming value when the concentration of a component is much higher than the TLV or even the median lethal dose (e.g., LD₅₀). The time dependence of the hazard index during the process should be considered for this purpose.

Only a few papers have described the application of the HI approach for the calculation of the total hazard during a PCO process [32,33]. For example, Dhada et al. [34] described the accumulative hazard effect for the permanent laboratory staff and graduate students in the context of benzene PCO over TiO₂. No information was presented for other types of VOCs or for the change in the hazard index during the PCO process when the intermediates formed. On the other hand, as shown in recently published papers [32,35], the effect of the formation of intermediates and byproducts during a PCO process is to be understood and minimized before an intense application of PCO method for indoor air purification.

Therefore, we decided to investigate the hygienic aspects of air purification using the TiO₂-mediated PCO method. This study aimed to evaluate the change in the total hazard as a function of irradiation time during the PCO purification process for various VOC pollutants, including acetone, alcohols, hydrocarbons, and heteroatomic compounds. According to the background from hygienists and scientists, the functions based on the hazard indexes, which consider the contributions of all the reaction components, were selected for the analysis of the total hazard. For this purpose, the photocatalytic oxidation of different types of VOCs over the TiO₂ photocatalysts was investigated, and special attention was given to the kinetics of the process, including a detailed analysis of the intermediate and final products. Based on the experimental data, the change in the total hazard during the PCO process using the hazard indexes was calculated as a function of the UV irradiation time. The type of oxidizing substrate has a substantial influence on the kinetics of hazard indexes. The TiO₂ modification with platinum results in a substantial decrease in the final hazard and increases the efficiency of air purification by the PCO method.

2. Experimental

2.1. Materials

The following chemical reagents were used as test organic substrates in the photocatalytic experiments: methanol (CH₃OH), ethanol (C₂H₅OH), propan-1-ol (C₃H₇OH), acetone (CH₃COCH₃), cyclohexane (C₆H₁₂), benzene (C₆H₁₀), acetonitrile (CH₃CN), diethyl sulfide (C₄H₁₀S, DES), and dimethyl methylphosphonate (CH₃PO(OCH₃)₂, DMMP). All the chemicals were high purity grade and used as received from AO REAHIM Inc. (Russia) without further purification.

Two commercially available TiO₂-powder photocatalysts, TiO₂ Hombifine N (from Sachtleben Chemie GmbH, Germany) and TiO₂ P25 (from Evonik Industries AG, Germany), were used for the photocatalytic oxidation of the organic substrates. In the paper, TiO₂ Hombifine N is referred to as TiO₂ HF.

The TiO₂ photocatalysts were modified with Pt to improve their photocatalytic activity against CO. For this purpose, 1%Pt/TiO₂ HF and 1%Pt/TiO₂ P25 samples were prepared via the chemical reduction of H₂PtCl₆. Typically, 5 g of TiO₂ HF or TiO₂ P25 was suspended in 50 mL of distilled water, and a certain aliquot of the H₂PtCl₆ solution was added dropwise. The suspension was stirred for 30 min to allow adsorption of the precursor on the TiO₂ surface. A three-fold molar excess of NaBH₄ was added dropwise to the suspension to reduce the metal precursor. After that, the suspension was stirred for 3 h. The precipitate was separated by centrifugation at 8000 rpm for 10 min and washed with distilled water. The centrifugation and washing procedures were repeated 10 times. Finally, the precipitate was dried in air at 120 °C overnight.

2.2. Kinetic experiments

The kinetic experiments were performed under static conditions at 25 °C in a 0.3 L batch reactor installed in the cell compartment of a Nicolet 380 FTIR spectrometer (Thermo Scientific, USA). The details of the experimental setup were described in the previous study [20].

Typically, the photocatalyst was uniformly deposited onto a 9 cm² glass support to obtain an even layer with a surface density of 2 mg/cm². The support was placed into the reactor and UV irradiated for 2 h to completely oxidize all the organic species adsorbed on the photocatalyst surface. A high-performance UV LED (Nichia, Japan), which provides light at λ_{max} ~ 373 nm and an irradiance of 10.2 mW/cm² in the UVA region, was used as the UV source.

After the photocatalyst pretreatment, the UV LED was turned off, and a certain aliquot of the organic substrate (i.e., 0.4 μL for DMMP, 0.5 μL for DES, 0.7 μL for acetonitrile, 0.8 μL for cyclohexane, and 1 μL for others) was injected into the reactor. Then, the UV LED was turned on again to initiate the photocatalytic oxidation. The irradiation continued until the total concentration of the C-containing products accumulated in the reactor reached the expected level calculated from the stoichiometric equation.

During an experiment, IR spectra were collected periodically to monitor the changes in the reactor. For example, Fig. 1a shows the evolution of the IR spectra during the photocatalytic oxidation of dimethyl methylphosphonate vapor. In addition to CO₂, which absorbs at 2230–2400 cm^{−1}, a number of narrow bands in region of 2040–2230 cm^{−1} indicate the formation of carbon monoxide as the oxidation product. The other absorption bands can be attributed to the organic intermediates formed during the PCO process.

Before the calculations, the raw IR spectra were modified by the subtraction of the spectrum for water vapor to remove the water bands in region of 1300–1900 cm^{−1} for a thorough analysis of other reaction components (e.g., Fig. 1b). The concentrations of the organic substrates and CO₂ were calculated from the collected IR spectra using the Beer-Lambert law as follows:

$$\int_{\omega_1}^{\omega_2} A(\omega) d\omega = \varepsilon \times l \times C \quad (4)$$

where $A(\omega) = \lg \left(\frac{I_0(\omega)}{I(\omega)} \right)$ is the absorbance, ω_1 and ω_2 are the limits of the corresponding absorption bands (cm^{−1}), ε is the coefficient of extinction (ppm^{−1}cm^{−2}), l is the optical path length (cm), and C is the concentration of a substance in the gas phase (ppm). The quantitative analysis of CO was performed using the method of spectral subtraction, which is based on the minimization of the spectrum length by subtracting the calibration CO spectrum from an experimental spectrum of the gas mixture [36]. The details of the performed calculations for multiple IR spectra can be found in the SI section.

2.3. Hazard indexes

The following functions were used to analyze the hazard during the photocatalytic oxidation of VOC:

(1) the THI index, which corresponds to the total hazard index and includes the impact of all the reaction components in the gas phase:

$$THI(t) = \sum_i \frac{C_i(t)}{C_i^{ref}} \quad (5)$$

(2) the MHQ index, which indicates the maximum hazard quotient among all the components and considers the “cocktail effect” of certain compounds (e.g., CO and SO₂, which are formed as the oxidation products during DES PCO):

$$MHQ(t) = \max \left\{ \frac{C_i(t)}{C_i^{ref}}, \sum_j \frac{C_j(t)}{C_j^{ref}} \right\} \quad (6)$$

The general expressions for the proposed functions are similar to the HI and HQ indexes mentioned in section 1, and the principal difference is the dependence of these indexes on the reaction time. The usage of two indexes allows us not only to determine the total hazard during the PCO process using THI but also to illustrate the contribution of different compounds to the total hazard using MHQ.

The reference concentrations (C_i^{ref}) used for the calculation of THI and MHQ are shown in Table 1. These data were selected from

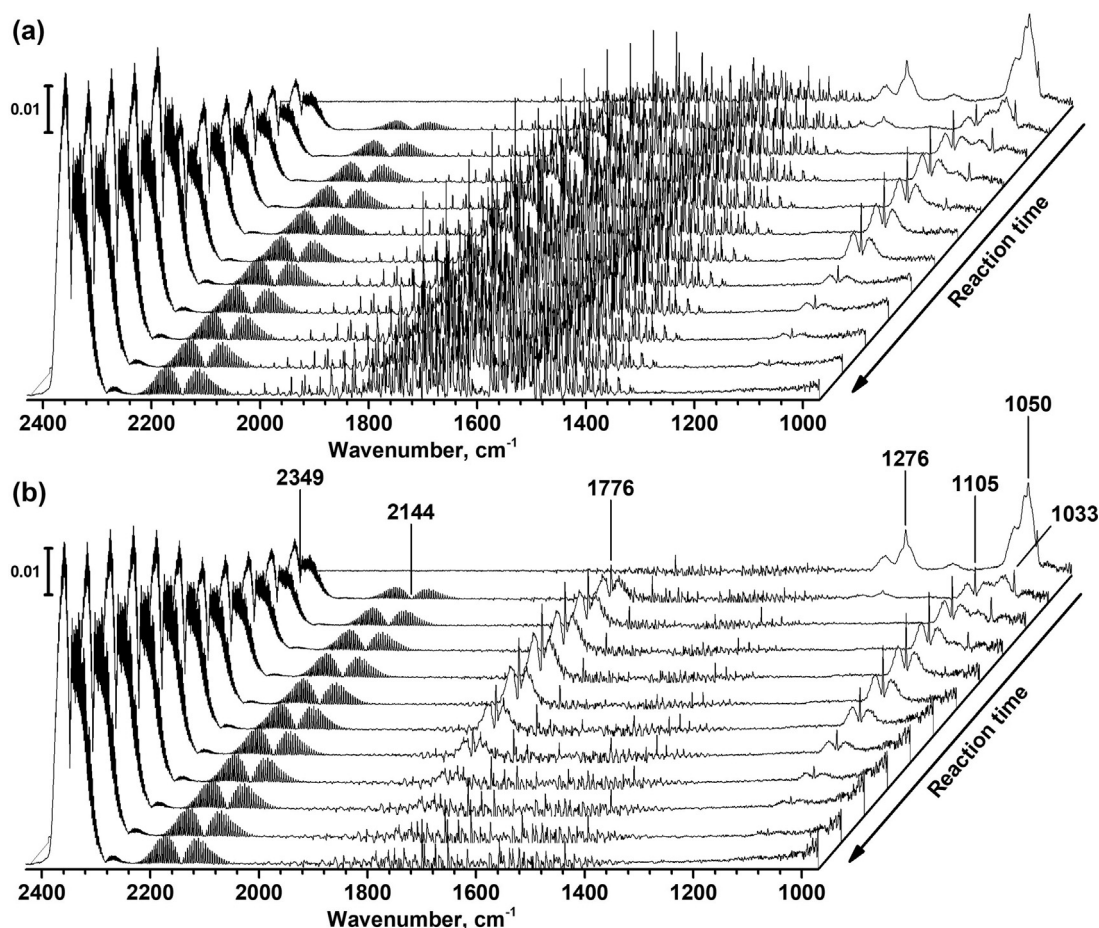


Fig. 1. Evolution of the IR spectra during the dimethyl methylphosphonate PCO over TiO_2 P25: (a) raw data; (b) after subtraction of the bands for water vapor. The other bands are attributed to the following compounds: DMMP (1276 and 1050 cm^{-1}), carbon dioxide (2349 cm^{-1}), carbon monoxide (2144 cm^{-1}), methanol (1033 cm^{-1}), and formic acid (1776 and 1105 cm^{-1}).

Table 1

Time-weighted average (TWA) and short-term exposure limit (STEL) values in the workplace from industrial standards for the UK (EH40/2005), Germany (TRGS 900), and the USA (ACGIH TLV) along with the reference concentration values used for the calculations.

Compound	CAS number	Workplace exposure limit					Selected reference concentration
		EH40/2005		TRGS 900	ACGIH		
		TWA	STEL	TWA	TWA	STEL	
		ppm	ppm	ppm	ppm	ppm	ppm
Acetaldehyde	75-07-0	20	50	50	–	25	20
Acetone	67-64-1	500	1500	500	200	500	200
Acetonitrile	75-05-8	40	60	20	20	–	20
Benzene	71-43-2	1	–	–	0.5	2.5	0.5
Carbon dioxide	124-38-9	5000	15000	5000	5000	30000	5000
Carbon monoxide	630-08-0	30	200	30	25	–	25
Cyclohexane	110-82-7	100	300	200	100	–	100
Dimethyl sulfide	75-18-3	–	–	–	10	–	10 ^a
Dimethyl methylphosphonate	756-79-6	–	–	–	–	–	1 ^b
Ethanol	64-17-5	1000	–	500	–	1000	500
Formic acid	64-18-6	5	–	5	5	10	5
Hydrogen cyanide	74-90-8	–	10	–	–	4.7	4.7
n-Hexane	110-54-3	20	–	50	50	–	20
Methanol	67-56-1	200	250	200	200	250	200
Nitrous oxide	10024-97-2	100	–	100	50	–	50
Propan-1-ol	71-23-8	200	250	–	100	–	100
Propanal	123-38-6	–	–	–	20	–	20
Sulfur dioxide	7446-09-5	–	–	1	–	0.25	0.25

^a TWA value of dimethyl sulfide (CAS number 75-18-3) is taken for diethyl sulfide (CAS number 352-93-2).

^b TWA value is taken from GOST 12.1.005-88 (Russia).

the TLV values for the workplace in the industrial standards for the UK, Germany, and the USA. The mentioned TLV values are also shown in Table 1. In most cases, the time-weighted average (TWA) limits were used as the reference concentrations due to their better representation of the standards and higher strictness compared to the short-term exposure limits (STELs). Additionally, the strictest value was selected among all the standards for different countries. No information about the TLV for dimethyl methylphosphonate was found in the industrial standards for the UK, Germany, and the USA, so the corresponding value was taken from the Russian GOST 12.1.005-88.

3. Results and discussion

In this study, we investigated the hygienic aspects of TiO₂-mediated PCO purification of air polluted with VOCs and analyzed the dependence of the hazard on time during the purification process. All the substrates studied can be divided into two groups. For the first group, the PCO process occurs without the formation of intermediates that can be detected in the gas phase. Acetone, methanol, cyclohexane, and benzene are included in the first group. For the second group, the PCO process occurs with the formation of one or more gaseous intermediates, which are further oxidized to their final products. Ethanol, propan-1-ol, acetonitrile, DES, and DMMP are included in the second group. The discussion of the results uses this division because the group affects the time dependence of the hazard indexes. Additionally, as will be shown below, the CO formed during the VOC PCO has a substantial effect on the final hazard after the PCO process. Therefore, the TiO₂ photocatalysts modified with platinum were considered in addition to bare TiO₂ to emphasize the importance of the photocatalyst modification.

3.1. Untreated TiO₂ photocatalyst

3.1.1. PCO without gas-phase intermediates

The first group contained substrates for which no intermediates were detected in the gas phase during the PCO process.

3.1.1.1. Acetone

Fig. 2a shows the kinetic plots for acetone removal due to adsorption and oxidation on the photocatalyst surface, as well as the accumulation of CO₂ and CO, which formed as the final oxidation products.

Liquid acetone (1 μ L) was evaporated into the reactor to give an initial acetone concentration of 1100 ppm. After the injection, the main portion of acetone adsorbed on the TiO₂ surface, and the acetone concentration before the UV LED was turned on was 440 ppm. The adsorption of the oxidizing substrate onto the photocatalyst surface is an indispensable step in the heterogeneous photocatalytic process. The contribution of the adsorption to the overall pollutant removal depends on the ratio between the photocatalyst surface (or mass) and the reactor volume. A higher ratio leads to a higher adsorption. Therefore, the adsorption step is considered along with the oxidation during the calculation of the hazard indexes. This approach may be described as placing a PCO air purifier into the closed chamber with the polluted air. In this context, all further changes in the gas mixture composition are the result of the PCO device working without dividing the adsorption and photocatalytic oxidation steps. The approach allows us to calculate the change in the hazard based on the change in the gas composition without considering specific experimental conditions (e.g., photocatalyst and reactor characteristics).

After turning on the UV LED at 6 min, the acetone was rapidly removed due to oxidation, and CO₂ and CO formed as the final oxidation products. Carbon oxides are the most widely observed final

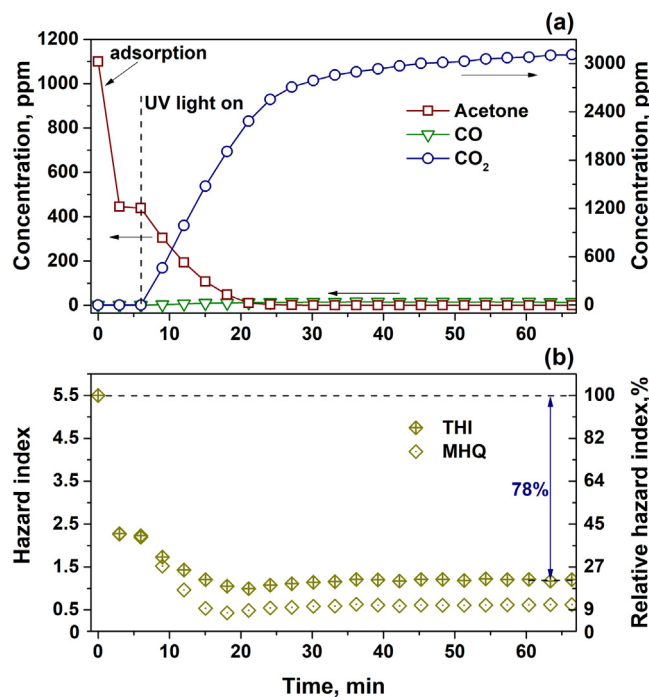


Fig. 2. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the acetone PCO over TiO₂ HF.

products of VOC oxidation, and they are unlikely to be adsorbed on the TiO₂ surface under the experimental conditions. No intermediates were detected in the gas phase. After 67 min, the CO₂ and CO concentrations reached a constant level of 3145 ppm and 15 ppm, respectively. These values correspond to an integral selectivity of 99.6% for CO₂ and 0.4% for CO.

Fig. 2b shows the time dependence of the calculated THI and MHQ indexes during the process. The selected reference concentration of acetone was 200 ppm (Table 1), which corresponds to an initial THI of 5.5. For the first 20 min, the THI index decreased because the acetone concentration decreased. After that, the THI slightly increased due to the accumulation of the final oxidation products (i.e., CO₂ and CO). The contribution of these compounds to the THI was similar because the MHQ at the end was 2 times lower than the THI – 0.6 and 1.2, respectively. The formation of CO as a by-product during PCO is a scientific challenge beyond the scope of this study, but some practical aspects of CO oxidation will be discussed later in section 3.2.

Therefore, the purification of air polluted with acetone vapor by photocatalytic oxidation results in a substantial decrease in the total hazard. To estimate the purification efficiency from a hygienic point of view, the THI was also calculated as a relative value (the right Y axis in Fig. 2b). In the case of acetone, the TiO₂ PCO process decreased the total hazard index by 78% compared to the initial value. This result allowed us to evaluate an acetone concentration limit, which corresponds to the THI of 1 at the end of the PCO process. The acetone concentration limit can be expressed as follows:

$$(7) c_{\text{acetone}}^{\text{lim}} = c_{\text{acetone}}^{\text{ref}} \times \frac{100}{100-78} = 910 \text{ ppm}$$

This means that if the acetone concentration in the polluted air does not exceed a value of 910 ppm, the air purification in the closed chamber (e.g., spaceship) by the PCO method is sufficient for human safety. If the hazard index is higher than 1, however, the air may lead to an adverse effect on human health. The details of the influence of the pollutant concentration on the final hazard index after the PCO process can be found in the SI section.

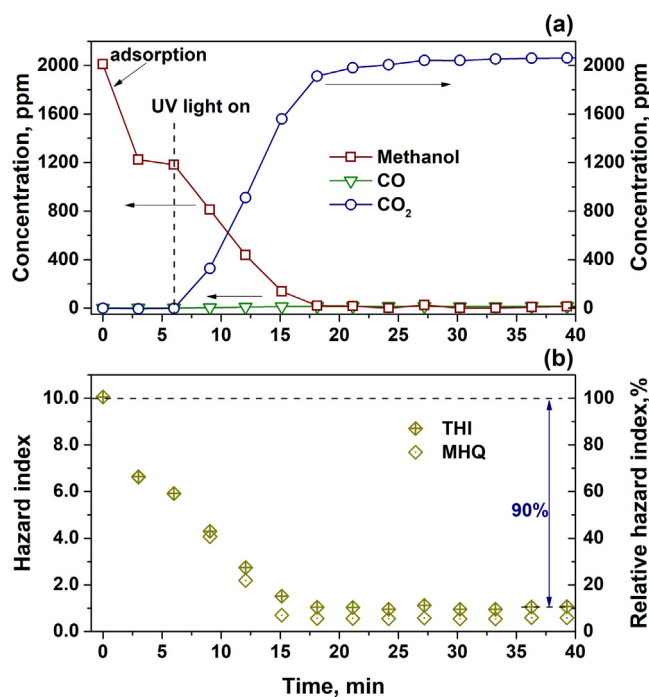


Fig. 3. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the methanol PCO over TiO₂ HF.

3.1.1.2. Methanol

Formaldehyde and formic acid are suggested to form during the photocatalytic oxidation of methanol [37,38]. No intermediates were detected under our experimental conditions, and methanol was rapidly and completely oxidized to CO₂ and CO. The kinetic plots for the reaction components and the hazard indexes during the methanol PCO are shown in Fig. 3. The situation is similar to the acetone PCO. The THI decreased from an initial value of 10 as the methanol concentration decreased due to the adsorption and photocatalytic oxidation. In addition, after that, the THI slightly increased due to the accumulation of CO₂, which was the main product, and CO traces (Fig. 3b). The total decrease in the THI at the end was 90% compared to the initial value. The contributions of CO₂ and CO to the final hazard were similar because the MHQ at the end of the process (i.e., 0.5) was the half of THI (i.e., 1.0).

3.1.1.3. Cyclohexane

The photocatalytic oxidation of cyclohexane occurs in a manner similar to the previous substrates but a much higher amount of CO is formed (Fig. 4a). The final CO concentration was 50 ppm, which corresponds to an integral selectivity of 1.5% towards CO₂, whose final concentration was 3360 ppm. CO has a substantially higher hazard compared with CO₂ (Table 1), and it has a stronger contribution to the THI after 50 min of the process even at a lower concentration. At the end of the process, the MHQ, which was from CO, was 2.0, and the THI was 2.6. The total decrease in the THI during the photocatalytic oxidation of cyclohexane vapor was 57% compared to the initial value.

3.1.1.4. Benzene

The TLV for benzene has an extremely low value of 0.5 ppm (Table 1). Therefore, an initial benzene concentration of 915 ppm, which results from the evaporation of 1 μ L of liquid benzene in the reactor, corresponds to a THI of 1830 (Fig. 5b).

After turning on the UV LED, the benzene concentration began to decrease with a constant rate until it was completely removed from the gas phase (Fig. 5a). The THI and MHQ values simultane-

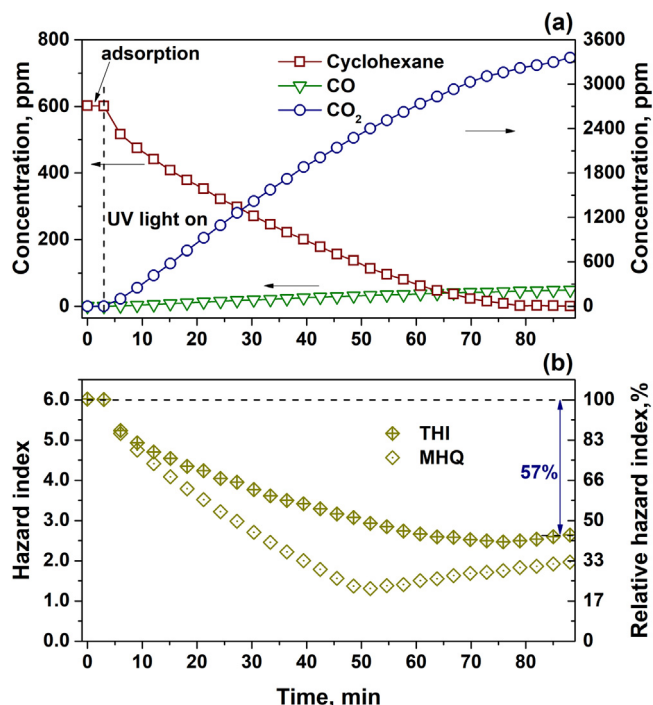


Fig. 4. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the cyclohexane PCO over TiO₂ HF.

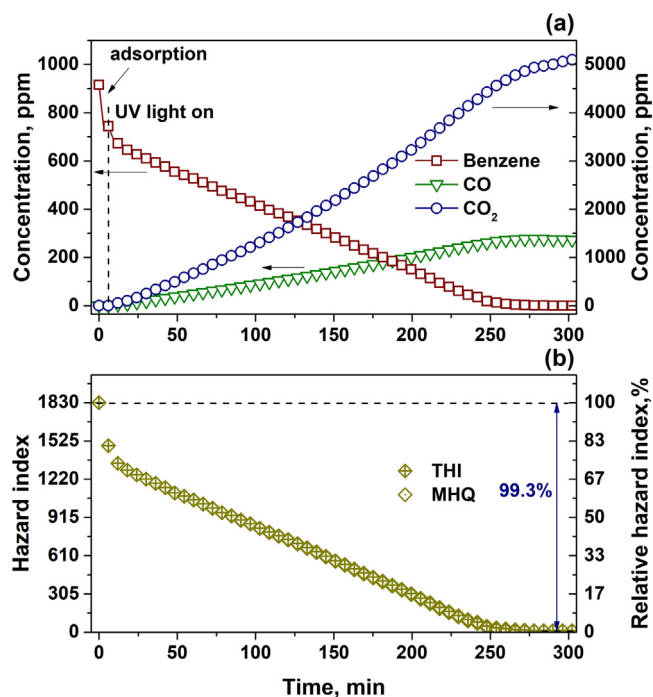


Fig. 5. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the benzene PCO over TiO₂ HF.

ously decreased as the benzene concentration decreased (Fig. 5b). During PCO, benzene was completely oxidized to CO₂ and CO without intermediates, which can be detected in the gas phase. The final value of THI was 11.9, which corresponds to 0.7% of the initial value. This indicated that the hazard of the gas mixture after the PCO process was ca. 150 times lower than that of the initial mixture, which contained only benzene vapor. CO, whose final concentration was

Table 2

Total decrease in the THI (Δ THI) during the PCO process and the predicted concentration limit calculated using Eq. (7).

VOC	Δ THI, %	Predicted concentration limit, ppm
Acetone	78	910
Methanol	90	2000
Cyclohexane	57	230
Benzene	99.3	70

270 ppm, was the main contributor to the final hazard. The final MHQ value due to CO was 10.8.

The results described above show the fundamental ability of the photocatalytic oxidation method to decrease the hazard of air polluted with VOCs. For all the substrates that can be photocatalytically oxidized without gaseous intermediates, the PCO process results in a substantial decrease (higher than 57% for the concerned substrates) in the hazard values. The THI and MHQ values had similar behaviors. They decreased as the concentrations of the initial pollutants decreased and slightly increased in the end mainly due to the accumulation of CO, which is a by-product of oxidation.

As mentioned above, a VOC concentration limit, which corresponds to a total hazard index of 1 at the end of the PCO purification process, may be useful for practical applications rather than the hazard decrease value. The predicted concentration limits for all the pollutants in the first group were calculated from the THI results (similarly to Eq. (7)) and are shown in Table 2. If the concentration of the VOC does not exceed the predicted limit value, the air purification in a closed chamber (e.g., spaceship) by the PCO method is safe for human health.

3.1.2. PCO with the formation of gas-phase intermediates

The second group of results obtained corresponds to the substrates, which produce gaseous intermediates upon photocatalytic oxidation.

3.1.2.1. Ethanol and propan-1-ol

In contrast to the previous substrates, the photocatalytic oxidation of ethanol vapor results in the accumulation of acetaldehyde in the gas phase, which further is completely oxidized to carbon oxides (Fig. 6a). Acetaldehyde, as well as other volatile aldehydes, has a low TLV (i.e., 20 ppm) and is more hazardous than ethanol (Table 1). For this reason, the calculated THI and MHQ values first decreased as the ethanol concentration decreased but then substantially increased as the acetaldehyde concentration increased in the gas phase (Fig. 6b). The final THI value, which corresponds to the maximum concentration of acetaldehyde, was ca. 10 times higher than the initial THI value. This result clearly indicated the potential risk of the PCO purification process due to the accumulation of partial oxidation products in the gas phase.

Further, acetaldehyde was completely removed from the gas phase via oxidation, and the THI and MHQ values simultaneously decreased. As a result, the total decrease in the THI value during the photocatalytic oxidation of ethanol vapor was 68% compared to the initial value. The final MHQ was 0.56, which corresponds to the 8 ppm of CO formed as a by-product of the oxidation.

Similar results were observed for the photocatalytic oxidation of propan-1-ol vapor (Fig. 7). The main intermediate of propanol PCO is propionaldehyde (or propanal). The kinetic plots for the reaction components and the hazard indexes were similar to those of ethanol and only differ in the actual values. The THI value, which corresponds to the maximum concentration of propanal, was 41% higher than the initial THI value, and the final THI was 89% lower than the initial one.

According to previously published papers [17,39,40], a general reaction pathway for the photocatalytic oxidation of n-alcohols is

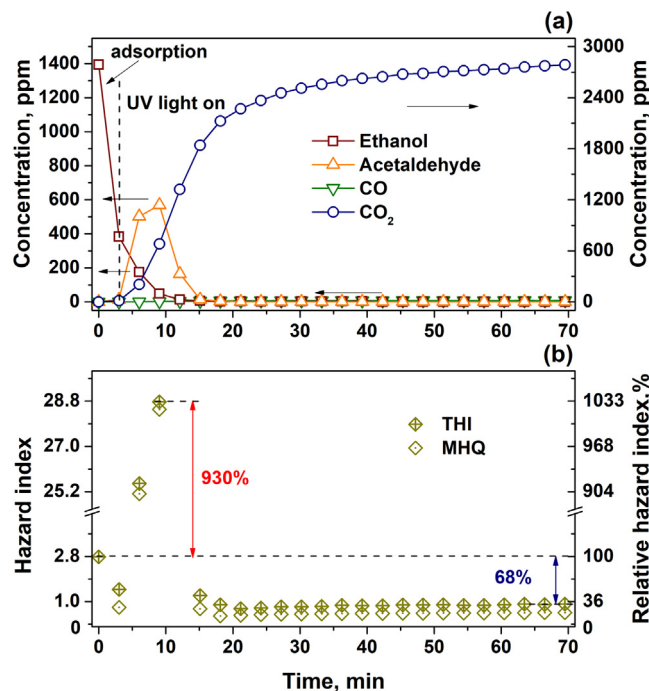


Fig. 6. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the ethanol PCO over TiO₂ HF.

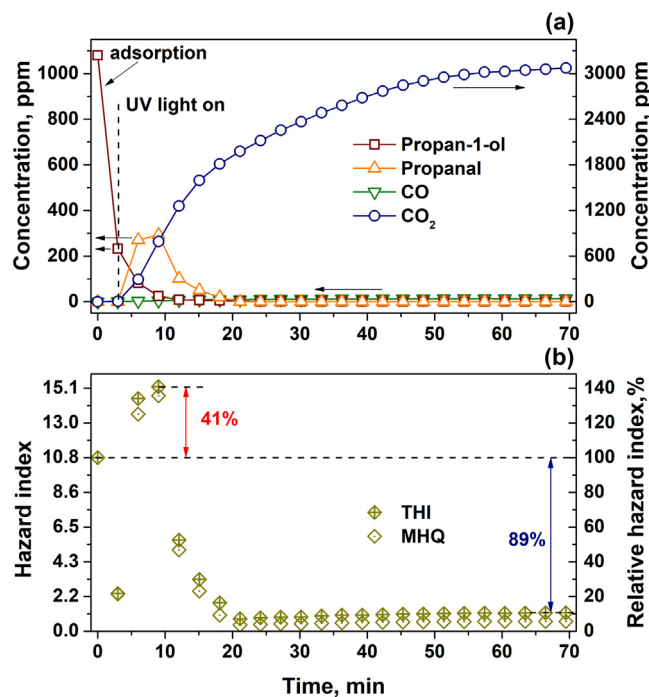


Fig. 7. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the propan-1-ol PCO over TiO₂ HF.

as follows: alcohols \rightarrow aldehydes \rightarrow acids \rightarrow shorter carbon chain aldehydes + alcohols \rightarrow CO₂ and H₂O (and CO traces). As shown above, the accumulation of aldehydes (e.g., acetaldehyde) is an important problem in the purification of air polluted with alcohols using the PCO method because it results in a substantial increase in the hazard. In this case, the PCO process may become a source of secondary pollution, and it will depend on the irradiation time (or the residence time under continuous-flow conditions). The potential danger linked to the carbonyl intermediate products, which

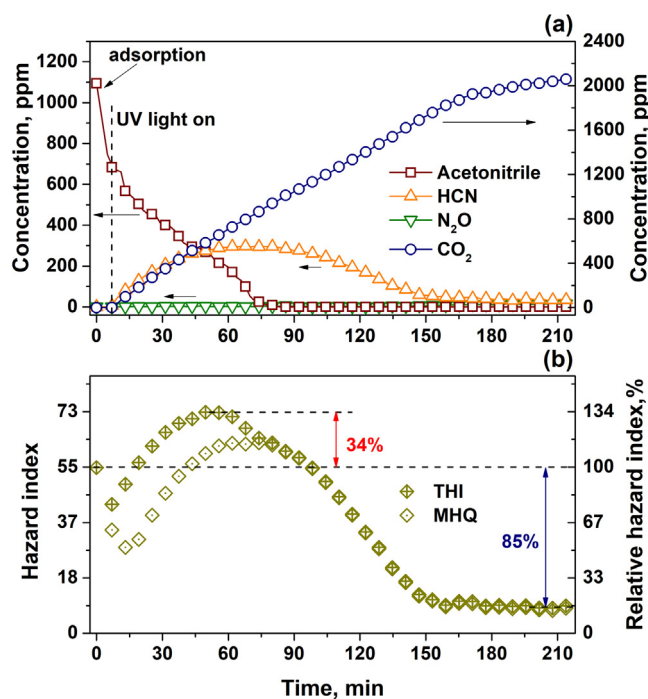


Fig. 8. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the acetonitrile PCO over TiO₂ HF.

may be released to the air during the PCO purification, has also been mentioned by Pierre Pichat in previously published papers [35,41].

3.1.2.2. Acetonitrile

Acetonitrile is another example of a substrate that produces gas-phase intermediates upon photocatalytic oxidation. Hydrogen cyanide (HCN) is the main intermediate during acetonitrile PCO. After turning on the UV LED, the acetonitrile concentration began to decrease due to its oxidation, and CO₂ and HCN accumulated in the gas-phase (Fig. 8a). The HCN concentration reached a maximum value of 300 ppm and further decreased due to its oxidation over the photocatalyst. On the other hand, HCN was not completely removed from the gas-phase, even after UV irradiation for 210 min, and its final concentration was 35 ppm. It can be assumed that a longer UV irradiation results in the complete removal of HCN.

The nitrogen from HCN transforms to the products, which remain on the photocatalyst surface (e.g., nitrates and cyanides), and to gaseous N₂O, which is the final oxidation product among CO₂, H₂O, and HCN. The final N₂O concentration was 15 ppm. It is important to note that the CO concentration, in this case, was lower than the detection limit.

Fig. 8b shows the kinetic plots of the calculated hazard indexes. The initial concentration of acetonitrile was 1100 ppm, which corresponds to a THI of 55. The THI decreased as the acetonitrile concentration decreased due to adsorption, but after turning on the UV LED, the THI began to increase due to the accumulation of HCN in the gas phase. The THI reached a maximum value of 73 at 50 min, which was 34% higher than the initial value, and decreased with further irradiation. It is important to note that after 80 min, the values of THI and MHQ were very close. This result indicated that HCN is the main contributor to the total hazard. Therefore, the formation of HCN as a by-product is an important problem for the purification of air polluted with acetonitrile by the PCO method. A long time period is required for complete air purification. In our case, the total decrease in the THI during the photocatalytic oxida-

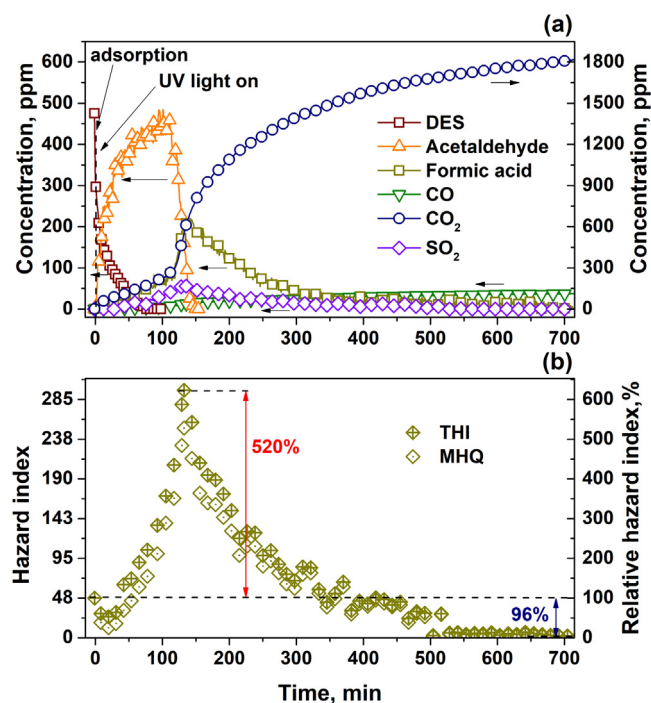


Fig. 9. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the diethyl sulfide PCO over TiO₂ HF.

tion of acetonitrile vapor was 85% compared to the initial value due to the incomplete oxidation of HCN.

3.1.2.3. Diethyl sulfide

Diethyl sulfide (DES) is a simulant for the well-known chemical warfare agent (CWA) bis(2-chloroethyl) sulfide, or mustard gas. DES is usually used for investigations to show the ability of the PCO method to clean up the aftermath of a terrorist attack using chemical weapons [19,42] because it has a much lower toxicity than mustard gas and simulates its chemical behavior well.

Several intermediates, including acetaldehyde, formic acid, and SO₂, were detected in the gas phase during the photocatalytic oxidation of DES (Fig. 9a). Acetaldehyde began to form immediately after turning on the UV LED. It had a very high concentration in the gas phase and accumulated until the complete removal of DES and the decomposition of sulfides on the photocatalyst surface. After that, the acetaldehyde concentration decreased rapidly. At the same time, an intense accumulation of formic acid was observed. In the end, the formic acid was completely oxidized to carbon oxides. The final concentrations of CO₂ and CO were 1810 and 37 ppm, respectively. In addition to organic intermediates, SO₂ was also detected in the gas phase during DES PCO. The main part of S from DES converts during oxidation to sulfates, which remain on the photocatalyst surface, and a small amount converts to SO₂, which is also completely oxidized to sulfates after long-term irradiation (Fig. 9a).

Fig. 9b shows the kinetic plots for the THI and MHQ values during the process. They are very similar to the plots for the ethanol PCO (see Fig. 6). All the detected intermediates (i.e., acetaldehyde, formic acid, and SO₂) have low reference concentrations (Table 1), and they result in a 6-fold increase in the THI compared to the initial value for the DES vapor only. The maximum THI and MHQ values were 296 and 250, respectively. SO₂ was the main contributor to the hazard among all the intermediates. It is important to note that according to Russian GN 2.1.6.1338-03, SO₂ and CO have a "cocktail effect", and this was considered during the MHQ calcu-

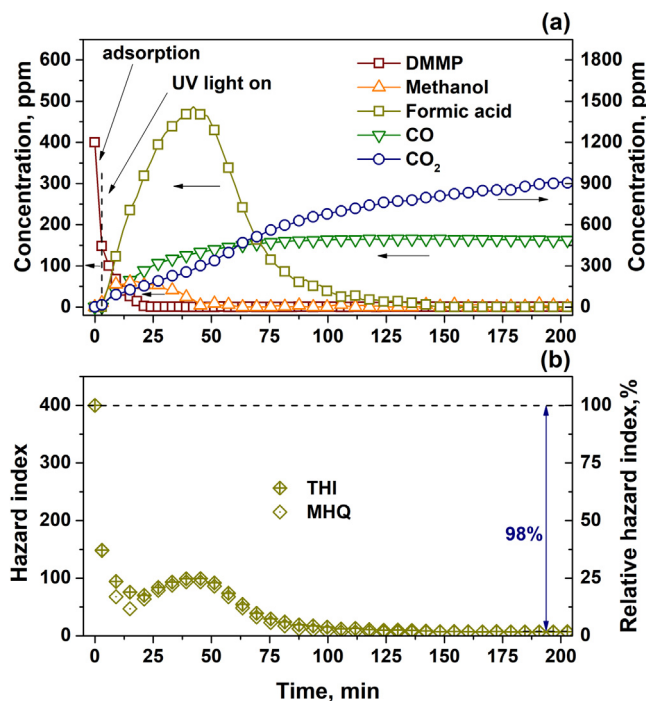


Fig. 10. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the dimethyl methylphosphonate PCO over TiO₂ P25.

lation. After 130 min, the hazard indexes began to decrease as the concentrations of formic acid and SO₂ decreased.

When all the intermediates were completely oxidized to the final products, the THI decreased to 2.1, which corresponds to a 96% total decrease compared to the initial value. The final MHQ value was 1.5 due to CO. The total THI decrease during the photocatalytic oxidation of DES was 96% compared to the initial value. Therefore, the photocatalytic oxidation of diethyl sulfide under long-term UV irradiation results in a substantial decrease in the total hazard.

3.1.2.4. Dimethyl methylphosphonate

Dimethyl methylphosphonate (DMMP) is another example of a CWA simulant. It is usually used to simulate sarin and soman agents. The photocatalytic oxidation of DMMP occurs through the formation of a large amount of formic acid and a small amount of methanol as intermediates (Fig. 10a). Under long-term UV irradiation, the intermediates were completely oxidized to carbon oxides. Carbon monoxide was a by-product, and its final concentration was 165 ppm, which corresponds to an integral selectivity of 15.3% towards CO₂.

DMMP is a hazardous compound with a TLV value of 1 ppm (Table 1). Therefore, the initial DMMP concentration of 400 ppm corresponds to a very high THI value (i.e., 400). The hazard indexes substantially decreased as the DMMP concentration decreased due to its adsorption and oxidation. The formic acid formed as an intermediate was responsible for the peak on the THI and MHQ kinetic plots (Fig. 10b). In contrast to the previous substrate, the THI during the process did not exceed the initial value for DMMP. Therefore, the purification of air polluted with dimethyl methylphosphonate by photocatalytic oxidation substantially decreased the total hazard. The final THI and MHQ values were 6.76 and 6.47, respectively. This result indicated that CO is the main contributor to the final hazard. The total decrease in the THI due to the PCO process was 98%.

Summarizing the data mentioned above, the PCO method resulted in air purification and decreased the total hazard of air polluted with VOCs. For the pollutants photocatalytically oxidized

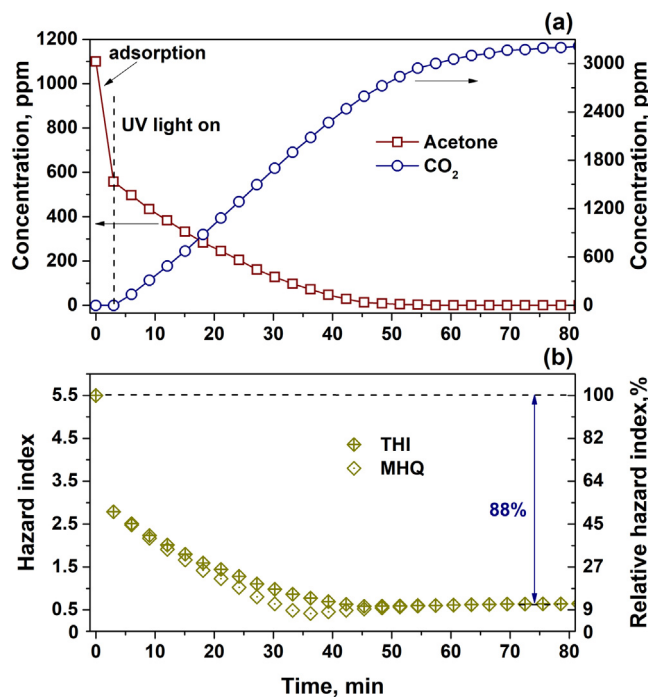


Fig. 11. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the acetone PCO over 1%Pt/TiO₂ HF.

without gaseous intermediates, the hazard indexes decreased as the concentration of the initial pollutant decreased and slightly increased at the end due to the accumulation of the products. Otherwise, for the pollutants that form gaseous intermediates upon photocatalytic oxidation, the hazard indexes increased during the process and were even higher than that of the initial pollutant. Under long-term irradiation, all the intermediates were completely oxidized, and the hazard indexes substantially decreased compared to the initial level.

3.2. TiO₂ photocatalyst modified with Pt

As shown above, the organic and inorganic intermediates and carbon monoxide, which is formed as a final by-product, are the main contributors to the increase in the hazard level during the PCO process. The prevention of intermediate accumulation in the gas phase requires further research. In this section, we focus on the problem of CO formation, which is the main reason for a high hazard index value at the end of the PCO process. To solve this problem, TiO₂ may be modified with nanoparticles of noble metals (e.g., Pt). This approach has been shown to prevent the formation of CO during the photocatalytic oxidation of VOCs [20] and result in catalysts with a high activity for CO photocatalytic oxidation under ambient conditions [43].

The kinetic plots for the PCO of acetone over 1%Pt/TiO₂ HF are shown in Fig. 11a. The main difference from the results on the unmodified TiO₂, which are shown in Fig. 2a, is that no CO was detected in the gas phase during the process. The final THI and MHQ values were the same because only CO₂ contributed to the final hazard (Fig. 11b).

The THI at the end of a PCO process can be used to evaluate the effect of the TiO₂ modification. The final THI values were 1.20 and 0.67 for TiO₂ HF and 1%Pt/TiO₂ HF, respectively, which corresponds to a 2-fold decrease in the total hazard index for the TiO₂ photocatalyst modified with Pt compared to the unmodified TiO₂. This result emphasizes the importance of photocatalyst modification with a metal to increase the air purification efficiency of the

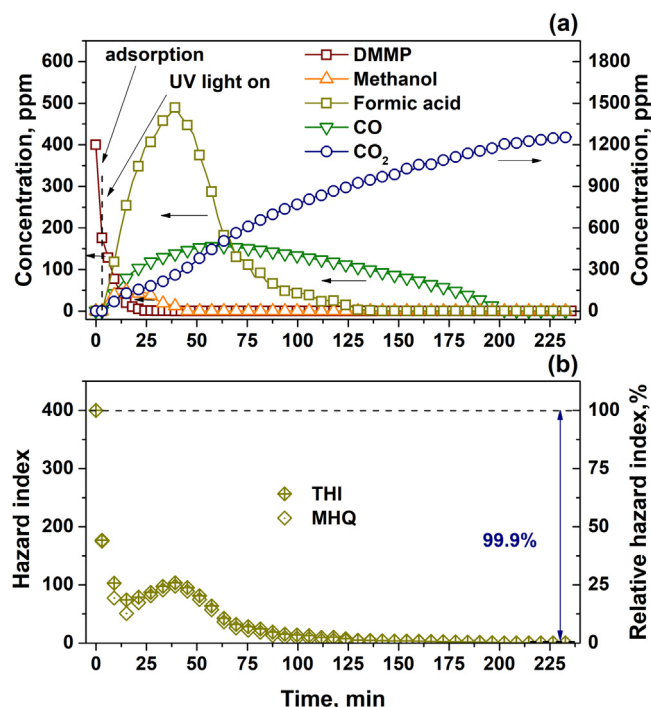


Fig. 12. Kinetic plots for the reaction components (a) and the hazard indexes (b) during the dimethyl methylphosphonate PCO over 1%Pt/TiO₂ P25.

PCO method. The total decrease in the THI for the PCO process over the TiO₂ photocatalyst modified with Pt was 88%.

As shown in section 3.1., the highest value for the selectivity of CO formation towards CO₂ formation was observed for the photocatalytic oxidation of dimethyl methylphosphonate. Therefore, this substrate was also selected for the investigation of TiO₂ modified with Pt. Fig. 12a shows the kinetic plots for the reaction components during the PCO of DMMP over 1%Pt/TiO₂ P25. All the detected intermediates and by-products were the same as the case of the unmodified TiO₂ P25 (Fig. 10a).

TiO₂ modification with Pt results in the suppression of the CO formation, but this effect was not as substantial as it was for the acetone PCO due to the more intense CO accumulation in this case. The maximum CO concentrations during the DMMP PCO over the 1%Pt/TiO₂ P25 and TiO₂ P25 samples were 156 and 165 ppm, respectively. However, it is important to note that in the case of 1%Pt/TiO₂ P25, the CO was completely oxidized under long-term UV irradiation (Fig. 12a). As a result, the final THI values were 0.26 and 6.76 for 1%Pt/TiO₂ P25 and TiO₂ P25, respectively, which corresponds to a 26-fold decrease in the total hazard index for the TiO₂ photocatalyst modified with Pt compared to the unmodified TiO₂. The ratio of these values emphasizes the critical effect of the presence of CO in a gas mixture on the potential hazard to human health. The total decrease in the THI due to the PCO process over the TiO₂ photocatalyst modified with Pt was 99.9%.

Thus, the application of a TiO₂ photocatalyst modified with Pt results in only CO₂ and H₂O being obtained as the final products during the photocatalytic oxidation of VOCs and increases the air purification efficiency of this method.

3.3. Concluding remarks

The THI and MHQ values used in this study are useful for the evaluation of the hazard of the initial gas mixtures and for the time-dependent calculations and related analyses. The THI requires capturing all possible compounds in the gas phase and, consequently, gives a stricter limitation for the air content. There-

fore, THI is more representative for the illustration of an integral hazard during the purification process. In general, the THI and MHQ values have similar behaviors, and the MHQ is useful for the determination of a key hazardous component of the gas mixture during the process.

This study addressed the oxidation of VOCs under static conditions, and the hazard calculations using the THI and MHQ indexes are also valid for the continuous-flow conditions. In the latter case, the residence time would be an analog of the irradiation time used for the static condition, and the outlet air composition after the PCO reactor and the final hazard will depend on the residence time. Therefore, all the results obtained for the static conditions can be extended to continuous-flow conditions by taking into account the residence time instead of the irradiation time.

4. Conclusions

Two indexes, the maximum hazard quotient (MHQ) and the total hazard index (THI), which is the sum of all the hazard quotients for all the air components, were used to analyze the hazard during air purification using a TiO₂-mediated PCO method. The following conclusions were made:

- (1) Based on the examples of various substrates, including acetone, alcohols, hydrocarbons, and heteroatomic compounds, the purification of air polluted with VOCs by the PCO method resulted in a substantial decrease in the hazard indexes under long-term UV irradiation.
- (2) For pollutants such as acetone, methanol, cyclohexane, and benzene, which are photocatalytically oxidized without the formation of gaseous intermediates, the hazard indexes decreased as the concentration of the initial pollutant decreased, and they slightly increased at the end of the PCO process due to the accumulation of oxidation products (i.e., CO₂ and CO).
- (3) For pollutants such as n-alcohols, acetonitrile, DES, and DMMP, which produce gaseous intermediates upon photocatalytic oxidation, the hazard indexes may increase during the PCO process and even be higher than that of the initial pollutant. C₁–C₃ carbonyl compounds (e.g., formic acid, acetaldehyde, propanal) and inorganic compounds (e.g., HCN, SO₂) were detected as intermediates in the gas phase and were responsible for an increase in the hazard indexes during the process due to their extremely low threshold limit values.
- (4) Carbon monoxide is a final by-product during the photocatalytic oxidation of VOCs and is responsible for the high hazard after the PCO process. The TiO₂ modification with noble metals (e.g., Pt) may result in the suppression of the CO formation during the process and a substantial decrease in the final hazard, which increases the efficiency of air purification by the PCO method.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.08.020>.

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